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<p>(54) Title: FIRE RETARDANTS</p> <p>(57) Abstract</p> <p>A fire retardant composition comprising: (i) at least one halogenated phosphate; and (ii) at least one phenol substituted with one or more halogen atoms. The fire retardant composition may be used in the production of plastic materials, as a fire retardant coating, and as a surface treatment to improve the fire retardancy of textiles and other fibres.</p>		

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- 1 -

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FIRE RETARDANTS

15 This invention relates to fire retardant compositions which have particular application as fire retardant agents in;

 (1) Plastic materials (such as polyurethanes, epoxy resins, and other thermoset, thermoplastic materials) and
20 precursors thereof.

 (2) Fire retardant coatings (including polymeric coatings) such as paints.

 (3) Surface treatments to improve the fire retardancy of textile yarns and fibres, in both synthetic
25 and natural fibres and in blends thereof.

 The invention is based on an unexpected synergistic or potentiating interaction between two hitherto known classes of fire retardants, namely (i) halogenated phosphates; and (ii) phenol substituted with one or more
30 halogen atoms. In particular, the combination of components (i) and (ii) produces a fire retardant having significantly superior fire retardant properties than either of the fire retardants alone, or based on a mere combination of their known properties.

35 According to one aspect of the invention, there is provided a fire retardant composition which comprises:

 (i) at least one halogenated phosphate; and

SUBSTITUTE SHEET

- 2 -

(ii) at least one phenol substituted with one or more halogen atoms.

Component (i) may be any halogenated phosphate which exhibits fire retardant properties. For example,

5 component (i) may be selected from

2-chloroethanol phosphate;

1-3-dichloro-2-propanol phosphate;

1-chloro-2-propanol phosphate;

2-3-di-bromo-1-propanol phosphate;

10 oligomeric chloroalkyl phosphonates;

bis(2-chloroethyl)2-chloroethyl phosphonate;

trichloroethyl phosphate (TCEP)

trichloropropyl phosphate (TCPP)

dimethyl monophosphate (DMMP).

15 TCEP and TCPP are particularly preferred.

Component (ii) may be selected from compounds containing one or more phenol rings which are substituted with one or more halogen groups, preferably bromine atoms. Compounds having a single phenol ring are
20 preferred is 2,4,6 tribromo phenol (TBP) is particularly preferred.

In a particularly preferred aspect of the invention there is provided a composition which comprises a mixture of:

25 (a) TCEP and/or TCPP: and

(b) TBP.

The precise weight ratio of component (i) to component (ii) is generally unimportant. For example, the ratio of component (i) to component (ii) may be from
30 1:0.45 to 1:1.25. Component (i) is generally a liquid, and component (ii) a solid. In a preferred embodiment of this invention, component (ii) is added to component (i) to form a saturated or substantially saturated solution, where the ratio of component (i) to component (ii) is
35 about 1:0.86. A diluent may be added to the mixture to allow component ratios greater than those that form a saturated solution.

SUBSTITUTE SHEET

- 3 -

The fire retardant composition of the invention is a liquid and does not appear to undergo any reactions at temperatures at least up to 73°C. At about 73°C the composition may change colour from a clear liquid to a darker colour (possibly due to bromine release). There appears to be an endothermic reaction at about 110°C.

The fire retardant composition is soluble in organic solvents such as methanol, ethanol, propanol, butanol, etc.; and is generally insoluble in aqueous solutions. Aqueous solutions may be prepared using commercial emulsifiers such as Teric (a registered trademark of ICI Australia Pty. Ltd.) and using techniques as described in the examples set out below.

When used as a fire retardant in plastics or resins, the fire retardant is blended with the components used to form the resin. For example, in the production of urethane resins or foams, the fire retardant may be mixed with a polyol component (i.e. a hydroxyl containing polymer, see Encyclopedia of Chemical Technology, 3rd Edition, Vol. 11, p. 88, John Wiley and Sons, 1981) prior to mixing of the polyol with an isocyanate to give a polyol blend. The polyol blend may, for example, contain from 5 to 80% of the fire retardant composition as hereinbefore described. The components of the polyol blend are suitable for storage for a considerable period of time, i.e., up to six months or more, even at elevated temperatures.

The polyol blend may additionally contain one or more basic materials, (such as an inorganic or organic base, for example an amine, such as trimethyl amine). When present, the base generally comprises from 0.01% to 15% (wt/wt) of the polyol blend. The polyol blend may also contain glycerol, silicone, water, CFC, an amine catalyst and a tin catalyst.

Alternatively, the fire retardant composition may be mixed with both the polyol and isocyanate at the same

SUBSTITUTE SHEET

- 4 -

time, to form a polyurethane polymer such as a polyurethane foam.

The amounts of reactants used in the preparation of urethane foams on a weight basis may vary considerably according to well known methods in the art.

Conventionally, the proportions of polyol and isocyanate are selected to provide approximately equal amounts (molar equivalents) of hydroxy and isocyanate functionalities, with isocyanate being in slight excess.

The fire retardant of the invention may constitute from 1 to 50% (wt/wt) of the reaction mixture.

Particular advantages associated with the use of fire retardant compositions of the invention in the production of polyurethanes are as follows:

1. The fire retardant enables high levels of fire retardancy to be achieved by the addition of the fire retardant into the precursors of polyurethane foam polymers.

2. The fire retardant exhibits plasticising effects which in part enable cell structures in foams to be easily modified and controlled.

3. The fire retardant is readily soluble in commercially available foam prepolymers and as such acts as a viscosity modifier.

4. Polyol blends containing the fire retardant of this invention are relatively stable.

The applicant has additionally found that where the fire retardant composition of this invention is used in the production of polyurethane foams, chlorofluorocarbons (CFCs) may be reduced or omitted from the reaction mixture. The fire retardant in accordance with this invention enables polyurethane foams to be controlled during their blowing phase utilising carbon dioxide gas, formed as a reaction between water and isocyanate, as a blowing agent, enabling the elimination or reduction of CFCs and other volatile agents. In this instance, the fire retardant of this invention also reacts as a

SUBSTITUTE SHEET

- 5 -

reaction temperature modifier to overcome the excessive rapid exotherm generated in polyurethane foams when the isocyanate components in the foam are reacted with water to form carbon dioxide.

5 In accordance with another aspect of the present invention, there is provided a polyol blend which comprises a polyol and a fire retardant composition as hereinbefore described, which is free of CFCs. Such polyol blends are generally used in the production of
10 polyurethane foams where the blends are reacted with an isocyanate to form the polymer, with carbon dioxide production in the reaction being the expanding gas.

In yet another aspect of the invention, there is provided a polyol blend which comprises a polyol, a fire
15 retardant as hereinbefore described, and low levels of CFCs. As used herein, the term "low levels" refers to 0.1% to 17% (wt/wt) of CFC in the polyol mix. Conventional polyol formulations generally contain 25% (wt/wt) CFCs or more. CFCs have been implicated in the
20 depletion of the ozone layer, and hence the use of low levels is advantageous. Polyol blends containing low levels of CFCs may also contain glycerol, silicone, water, an amine, and a tin catalyst. The polyol blend may contain from 5 to 80% of the fire retardant
25 composition as hereinbefore described.

This invention also relates to polyurethane foams which incorporate fire retardants as described herein; and further relates to polyurethane foams when produced by the reaction of a polyol blend containing a fire
30 retardant, with an isocyanate containing compound.

In accordance with another aspect of this invention, the fire retardant compositions described herein may be incorporated into polymeric materials such as polyvinyl chloride (PVC), polyester, polyamide, polyimide,
35 polypropylene, polyethylene, nylon, phenolic resin and acetal resin. Such polymeric materials may contain from 0.1 to 50% (wt/wt) of the fire retardant composition of

SUBSTITUTE SHEET

- 6 -

this invention. The fire retardant of this invention is simply added to the various reaction mixtures which give rise to above polymeric material. The fire retardant is thus incorporated into the polymeric matrix. The fire
5 retardant may react to some extent with the components of the reaction mixtures, as long as polymerization or conventional properties of the polymers are not adversely effected.

The fire retardant of this invention may also be
10 incorporated into a pulp of cellulose or like fibres for the production of paper, cardboards, etc. Such material exhibits fire retardant properties.

When used as a fire retardant coating or surface treatment, the fire retardant composition may be diluted
15 with an organic solvent to form, for example, a mixture contains 1% to 90% (wt/wt) fire retardant, and then sprayed onto a surface which is desired to be coated. On evaporation of the organic solvent, a stable surface coating remains. In the treatment of exposed timber
20 products, for example, the fire retardant may be incorporated into conventional wood stains to yield a decorative surface. In another instance, for example, compositions of this invention may be applied to furnishings, drapes, carpets, tents, screen cloths, etc
25 to impart fire retardancy. In such cases a stain release, deodorant and the like may be added to the mixture. The term "deodorants" used herein refers to any compound or number of compounds which have an odour reducing effect, or which impart a pleasant smell to the
30 human and/or animal nose. Deodorants or odour modifiers are described, for example, in the Encyclopedia of Chemical Technology, 3rd Edition, Vol. 16, pp. 297-305, John Wiley & Sons, 1981.

In the case of surface treatments of textiles, yarns
35 and fabrics it is generally preferred to use an aqueous fire retardant. This is formed by the combination of the compound with a commercial emulsifying agent (such as ICI

SUBSTITUTE SHEET

- 7 -

Teric 200), which is then diluted with water and applied to the fabric or textiles. Application may be by immersion and nip roller to achieve pick up weights of between 20 -90%. Usually a high temperature treatment (such as about 100°C-250°C) of the fabric follows application of the compound to stabilise both the compound and the fabric. The resultant cloth exhibits a high degree of fire retardancy. (See Example).

Particular advantages associated with the use of the fire retardant compositions in relation to fabric applications of the invention are;

1. A good "hand" of feel of the fabric. Many fire retardants effect the feel of fabrics causing them to feel stiff or "woody".
2. Good light-fastness, the treated fabric exhibits uv stability well in excess of required standards.
3. A high level of wash retention, again well in excess of standards.
4. Ease of application, that is requiring a single treatment.

In accordance with another aspect of this invention, there is provided a fire retardant composition as defined herein, which additionally comprises one or more of the following:

- (i) a deodorant;
- (ii) stain release compound;
- (iii) wood stain or paint;
- (iv) volatile organic solvent and/or inorganic solvent; and/or
- (v) emulsifying agent.

In accordance with a further aspect of this invention, there is provided textiles; yarns; fabrics; timber; wood-containing products; or articles such as carpets, screen cloths, drapes or furnishings; which have been treated with a fire retardant composition as described herein. By the term "treatment" is meant

- 8 -

application by spraying, dipping, painting and other methods well known in the art for the application of fire retardants.

A number of embodiments of the present invention will now be further described, with reference to the following, non-limiting example. It is to be understood that the following examples in no way restrict the invention to those compounds, compositions and methods specifically exemplified, which are detailed by way of representative example only.

EXAMPLE 1

Preparation of Fire Retardant Compositions:

Reagents:

- 15 (i) Trichloropropyl phosphate (TCPP) and trichloroethyl phosphate (TCEP) were obtained commercially from Akzo Chemicals under the trade names FYROL Pcf and FYROL Cef respectively. Both TCPP and TCEP are liquids at ambient temperatures.
- 20 (ii) Tris 2,4,6 tribromophenol and Bis 2,4,6 Tribromophenol (TBP) were obtained from either Great Lakes Chemical Company, West Lafayette, Indiana, U.S.A. or from Bromine Compounds Limited, Beersheva, Israel. These compounds are flaky solids at ambient temperatures.
- 25 Fire retardant compositions were prepared by mixing the brominated phenol with one or both of chlorinated phosphates, until all the brominated phenol is dissolved therein. Warming the chlorinated phosphate, for example to 70°C, promotes solubility of the brominated compound.
- 30 Where TCPP and TCEP are used in combination, the weight ratio is usually 1:1 however this may vary.

A range of fire retardant composition were prepared wherein the weight ratio of chlorinated phosphates (TCPP and TCEP) to brominated phenols was from 1:0.45 to 1:1.25. For Examples 2 to 6 listed below a near saturated solution of fire retardant was prepared by dissolving 80g of TBP in 100g of TCPP.

SUBSTITUTE SHEET

- 9 -

EXAMPLE 2**Polyol Blends (stability of blends containing fire retardant):**

The following components were mixed together in a standard commercial mixer, or beaker, to give a common polyol blend:

- 31.5g Polyol - Daltolac 140 (trademark of ICI Chemical Industries Limited)
- 2.29g Glycerol
- 10 - 0.67g Silicon - Dow Corning DC 193
- 0.44g Amine - Dabco 33LV (33% trimethyl amine)
- 0.4g Water
- 0.04g Tin - Dabco T12 catalyst (Dibutyl tin dilaurate)
- 15 - 14.57g CFC - Dupont Freon 11
- 53.00g Fire retardant composition of Example 1.

Polyol blends containing no CFCs were prepared by deleting the CFC component in the above mix, and raising the amount of water to 2.44 g.

- 20 The above formulations contain 50.5% (wt/wt) fire retardant. Formulations the same as above (in the presence and absence of CFC) were prepared which contain from 5 to 63% (wt/wt) fire retardant.

- 25 The above polyol formulations were stable, and could be stored for at least 60 days at elevated temperatures of 60°C without any noticeable deleterious effects. Parameters checked include changes in both the viscosity and the colour of the blend and, when reacted with an isocyanate, changes in the reaction time profiles of,
- 30 Cream, Rise & Gel times (as described in the Polyurethane Handbook, Hansen Publishers, New York, 1985, Ed. Gunter Oertel), when compared with fresh blends of the same formulation. No noticeable changes were observed.

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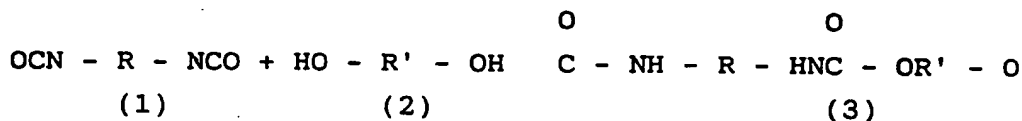
SUBSTITUTE SHEET

- 10 -

EXAMPLE 3**A Standard Polyurethane Blend with Varying Levels of Fire Retardant (Example 1) Compared to a Commonly Used Fire Retardant (Fyrol Pcf):**

5 Polyurethane foams are prepared by reacting a hydroxyl-containing polymer (polyol) with a polyfunctional isocyanate as shown in Scheme A, where (1) is polyfunctional isocyanate, (2) a polyol, and (3) a polyurethane

10

Scheme A:

15 wherein R and R' are alkyl, alkoxy or the like optionally substituted with one or more substituents.

A detailed review of polyurethanes is to be found in Polyurethane Elastomers, by C. Hepburn, Applied Science Publishers, 1982, which is incorporated herein by
20 reference.

Polyurethane foams were produced by mixing the polyol formulations with a polyisocyanate, SUPRASEC 5005 (a diisocyanato-diphenylmethane), obtained from ICI Australia Operations Limited. The amount of isocyanate
25 used to react with the polyol was calculated by determining the total equivalents of hydroxyl groups in the polyol formulation, according to methods well known in the art, and described for example in Polyurethane Elastomers by C. Hepburn, Supra.

30 Conventionally, the isocyanate is used in very slight excess. An index of x 1.05 is commonly used. Thus, the polyol blend of Example 2 would be mixed in a commercial mixer with 56 g of isocyanate. (Suprasec 5005) The following formulations were produced:

35	3a	3b	3c	3d
Daltolc 140	31.50	31.50	31.50	31.50
Glycerol	2.29	2.29	2.29	2.29
Silicone	0.67	0.67	0.67	0.67

- 11 -

	3a (cont)	3b (cont)	3c (cont)	3d (cont)
Amine	0.44	0.44	0.44	0.44
Tin	0.04	0.04	0.04	0.04
5 Water	0.44	0.44	0.44	0.44
CFC (F11)	14.57	14.57	14.57	14.57
Example 1	0	0	5.60	0
Fyrol Pcf	0	5.60	0	21.00
Isocyanate	56.00	56.00	56.00	56.00
10				
	3e	3f	3g	3h
Daltolc 140	31.50	31.50	31.50	31.50
Glycerol	2.29	2.29	2.29	2.29
Silicone	0.67	0.67	0.67	0.67
15 Amine	0.44	0.44	0.44	0.44
Tin	0.04	0.04	0.04	0.04
Water	0.44	0.44	0.44	0.44
CFC (R11)	14.57	14.57	14.57	14.57
Example 1	21.00	0	31.00	53.00
20 Fyrol Pcf	0	31.00	0	0
Isocyanate	56.00	56.00	56.00	56.00

* All quantities are in grams.

Formulation 3a contains no fire retardant.

- 25 Formulations 3c, 3e, 3g and 3h contain increasing amounts of the fire retardant composition of this invention. Formulations 3b, 3d and 3f contain increasing amounts of the commercially available fire retardant Fyrol Pcf (trichloropropyl phosphate).

- 30 On reaction the various formulations gave rise to polyurethane foams.

TESTS

Limited Oxygen Index ANSI/ASTM D 2863-77:

- 35 This test, is an Australian and International Standard of flammability (see Polyurethane Handbook, Ed. Gunter Oertel, 11985, Carl Hanser Verlag, pp. 495-496).

SUBSTITUTE SHEET

- 12 -

Basically, the test measures the % of oxygen that will support candlelight combustion. The lower the % oxygen index the more flammable is a material.

5 Results:

	% Oxygen Index
Blend 3a, (no fire retardant)	19.5
Blend 3b (5.6g)(Conventional formulation)	22.5
Blend 3c (5.6g)	23.0
10 Blend 3d (21g)(unstable foam)	23.5
Blend 3e (21g)	24.6
Blend 3f (31g)(unusable foam)	25.0
Blend 3g (31g)	27.5
Blend 3h (53g)	28.5

15 These results show that foams produced using conventional fire retardants have a lower percentage oxygen index, and thus are more flammable than those foams produced utilising the fire retardant composition of this invention. It is to be noted that small
20 increases in the percentage in oxygen index correspond to significant increases in fire retardancy. For example, a difference of 0.5 in the percentage oxygen index between formulation 3b (containing a conventional fire retardant) and formulation 3c (containing the fire retardant
25 composition of this invention) is indicative of a significant decrease in flammability of the foam produced by composition 3c.

 The increase in fire retardancy observed in foams containing the fire retardant composition of Example 1 is
30 believed to result from a synergistic interaction between the components of the fire retardant, namely TCPP and TBP.

 The foam produced from blends 3b, 3d and 3f, was inferior when compared to foams produced using the same
35 level of the fire retardant of the invention, insofar as flammability and stability are concerned.

 Formulations according to blends 3b, 3d and 3f were

- 13 -

also produced, where the fire retardant Fyrol Pcf was replaced with halogenated phosphates, trichloroethyl phosphate (TCEP), and dimethylmono phosphate (DMMP), and with tribromophenol (TBP). The percentage oxygen index of the foams produced using halogenated phosphates generally corresponded to those obtained using the fire retardant Fyrol Pcf (TCPP). The foams produced using TBP were of very poor quality and possessed a very low percentage oxygen index, below about 19.

These results show that the combination of a halogenated phosphate and a phenol substituted with one or more halogen atoms interact synergistically to produce foams having decreased flammability, when compared to foams produced using either of the components alone.

These results are surprising and unexpected.

The formulation of Example 1 was advantageous as stable foams could be produced in the presence of large quantities of fire retardant (see blends 3g and 3h). In contrast, formulations containing more than 21 g of Fyrol Pcf or other halogenated phosphates were physically inferior (poor dimensional stability and low closed cell count) and gave rise to unstable foams. Foams produced using the fire retardant TBP were of very poor quality and were generally unstable regardless of the amount of TBP used.

The improved stability of foams produced using the fire retardant composition of Example 1 was unexpected, particularly as the independent components of the fire retardant of Example 1 did not give rise to stable foams when large quantities were used (blends 3d and 3f).

Large quantities of the fire retardants of this invention may be incorporated into polyurethane foams without disturbing their structure. This is advantageous as foams which are highly flame resistant may be produced.

SUBSTITUTE SHEET

- 14 -

EXAMPLE 4**Soluble Fire Retardants:**

The fire retardant composition of Example 1 was diluted in methanol to give 20% (w/w) fire retardant composition. This material was sprayed onto needled polypropylene (a ribbed wall covering manufactured by Melded Fabrics Pty Ltd of Melbourne) and allowed to dry. Dry pick up weight was 15.7%

The material was then washed 10 times with hot water containing a detergent.

The treated material exhibits excellent fire retardancy as measured by ASTM method FMVSS 302, a horizontal burn test (see - International Plastics Flammability Handbook, Author Jurgen Troitzsch, published by Hanser Publishers ISBN 3-446-13571-5, Section 8.3.1.2). In this test, a slab of material 8 inches x 3 inches was held horizontally in a flame and the rate of burn back measured. Results classify samples in this test as "Self Extinguishing". The treated material did not burn.

In contrast, non-treated material was completely consumed by flame, which rapidly spread down the strip of material.

Needled polypropylene treated in the same manner (including washing) as above, with equivalent amounts of TCPP, TCEP, DMMP or TBP shows significant burn back (about 83 mm/minute) and consumption of material.

EXAMPLE 5**Fire Retardant Coating For Timber:**

In this example samples of 6mm Plywood (200mm by 200mm) were thoroughly dried by placing them in an oven at 60 Deg C for 24 hours prior to the test. One half of each sample is liberally coated on both sides with a mixture comprising 20 parts of Example 1 and 80 parts of 1,1,1, trichloroethane (solvent) and allowed to dry. Other samples were also made at the same time and in a

- 15 -

- similar manner using no fire retardant, and equivalent amounts of the fire retardants TCEP, TCPP, DMMP and TBP. After drying the samples were cut into 10mm wide strips so that the sample size is 6mm by 10mm by 200mm with
- 5 approximately one half of the sample (10 by 100mm) having a coating of fire retardant. The samples were then held downwards at an angle of 45 Deg with the untreated end in the lower aspect. The untreated end of each sample was lit. Burning is observed as the flame travels upward.
- 10 In the case of those samples treated with the fire retardant of Example 1, burning ceased upon the flame reaching the treated area. In all the other samples tested, complete burning took place with the samples being consumed.

15

EXAMPLE 6**As a Surface Treatment for Textiles:**

- In one example a mixture is formed with 85% of the fire retardant compound (Example 1) and 15% Teric 200 (ICI). The Teric 200 is heated to 50 Deg C to liquify it and the fire retardant is slowly added whilst the temperature is kept at 50 dec C. This is then allowed to cool. This mixture is further added to water at the rate of 200 grams per litre, with constant agitation.
- 20
- 25 The fabric to be treated is immersed in the solution and run through nip rollers to give a pick up weight of between 40 to 100% (usually 70%). In some instances a stain release, deodorant, uv stabiliser or other treatment may be added to the mixture. The wet fabric is
- 30 then stretched and exposed to hot air at between 120 and 160°C for several minutes.

TESTS

- 35 Australian Standard 1530 (parts 2 & 3) TESTS FOR FLAMMABILITY OF MATERIALS AND SIMULTANEOUS DETERMINATION OF IGNITION, FLAME PROPAGATION, HEAT RELEASED AND SMOKE INDEX

This is an Australian standard test (for a detailed

SUBSTITUTE SHEET

- 16 -

reference, see International Plastics Flammability Handbook, Author Jurgen Troitzsch, published by Hanser Publishers ISBN 3-446-13571-5 Section 8.2.16 which is incorporated herein by reference) and in these examples
5 testing was carried out at the Australian Wool Testing Authority Ltd. North Melbourne, Victoria, Australia.

In one sample tested against the AS 1530 part 2 test (a vertical burn test; flame applied to the bottom of a strip of material) the following test results were
10 obtained:

Sample: Woven fabric comprising 65% polyester and 35% cotton having a nominal mass of 220 grams per square metre, colour navy.

Dry pick up weight of fire retardant active
15 ingredients as per Example 6 was 10.8%

Results: (AWTA test # 7-428445-fn)

	<u>Treated</u>	<u>Untreated</u>	<u>Result range</u>
Speed Factor	0	44	0-60
20 Spread Factor	0	23	0-40
Heat Index	1	12	0-Upwards
Flammability Index	1	85	0-100

In these tests, high values reflect undesirable
25 results. It is clear from the above data that treatment with the fire retardant is most advantageous.

In another sample tested against the AS 1530 part 3 test (sample moved towards a radiant heat source) the following test results were obtained:

30 Sample: Woven fabric comprising 100% wool having a nominal mass of 388 grams per square metre and a thickness of 1.3 mm.

Dry pick up weight of fire retardant active ingredients as per Example 6 was 11.3%.

35 The test is a comparison between unwashed material and material washed ten times with hot water and detergent.

SUBSTITUTE SHEET

- 17 -

Results: (AWTA test # 7-428995 fn)

	<u>Unwashed</u>	<u>Washed</u>	<u>Result range</u>
Ignitability	0	0	0-20
Spread of flame	0	0	0-10
5 Heat evolved	0	0	0-10
Smoke developed	5	4	0-10
Number of specimens tested = 6			
Number of specimens ignited = 0			

10 Again, these results show that the treated material
after washing is still highly fire resistant.

15 The described compositions and methods have been
advanced merely by way of explanation and many
modifications may be made thereto without departing from
the spirit and scope of the invention which includes
every novel feature and combination of novel features
herein disclosed.

SUBSTITUTE SHEET

- 18 -

CLAIMS:

1. A fire retardant composition which comprises:
 - (i) at least one halogenated phosphate; and
 - (ii) at least one phenol substituted with one or more halogen atoms.
2. A fire retardant composition according to claim 1, wherein the halogenated phosphate is selected from 2-chloroethanol phosphate; 1-3-dichloro-2-propanol-phosphate; 1-chloro-2-propanol phosphate; 2-3-di-bromo-1-propanol phosphate; oligomeric chloroalkyl-phosphonates; bis(2-chloroethyl)2-chloroethyl-phosphonate; trichloroethyl phosphate; trichloropropyl-phosphate or dimethyl monophosphate.
3. A fire retardant composition according to claim 1, wherein the halogenated phosphate is selected from trichloroethyl phosphate or trichloropropyl phosphate.
4. A fire retardant composition according to claim 1, wherein the phenol substituted with one or more halogen atoms comprises a single phenol ring substituted with one or more bromine atoms.
5. A fire retardant composition according to claim 4, wherein the phenol substituted with one or more halogen atoms is 2,4,6,tribromophenol.
6. A fire retardant composition according to claim 1 which is a substantially saturated solution.
7. A fire retardant composition according to any one of claims 1 to 6 which additionally comprises one or more of the group selected from a deodorant, stain release compound, wood-stain, paint, volatile organic solvent and emulsifying agent.

SUBSTITUTE SHEET

- 19 -

8. A polyol blend which comprises a hydroxyl containing polymer (polyol) and a fire retardant composition according to any one of claims 1 to 6.

9. A polyol blend according to claim 8 which additionally comprises one or more basic compounds.

10. A polyol blend according to claim 9 which the basic compound is an amine.

11. A polymeric blend according to any one of claims 8 to 12 which is free of chlorofluorocarbons (CFCs).

12. A polyol blend according to any one of claims 8 to 12 which additionally comprises 0.1% to 17% chlorofluorocarbons.

13. A polyurethane foam which incorporates a fire retardant according to any one of claims 1 to 6.

14. A polyurethane foam when produced by reacting a polyol blend according to any one of claims 8 to 12 with an isocyanate compound, in the presence of water and one or more catalysts.

15. A polymeric material which incorporates a fire retardant composition according to any one of claims 1 to 6.

16. A polymeric material according to claim 15 selected from a polyurethane, epoxy resin and thermoset thermoplastic material.

17. A polymeric material according to claim 11 wherein the polymeric material is a polyvinyl chloride,

SUBSTITUTE SHEET

- 20 -

polyester, polyimide, polypropylene, polyethylene, nylon, phenolic resin or acetal resin.

18. Textiles, yarns and fabrics treated with a fire retardant composition according to any one of claims 1 to 6.

19. Timber and wood-containing products treated with a fire retardant composition according to any one of claims 1 to 6.

20. A pulp of cellulose or like fibres which contains a fire retardant according to any one of claims 1 to 6.

21. Paper or cardboard which contains a fire retardant according to any one of claims 1 to 6.

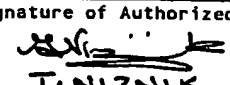
22. An article treated with a fire retardant according to any one of claims 1 to 6, which article is a carpet, tent, screen cloth, drape or furnishing.

23. A process for treating an article with a fire retardant composition, which process comprises mixing the fire retardant composition of any one of claims 1 to 6 with an emulsifying agent, and thereafter applying the thus formed composition to the article.

24. A process for treating an article with a fire retardant, which process comprises mixing a fire retardant according to any one of claims 1 to 6 with an organic solvent and thereafter applying the mixture to the article desired to be treated.

INTERNATIONAL SEARCH REPORT

International Application No. **PCT/AU 90/00275**

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) 6				
According to International Patent Classification (IPC) or to both National Classification and IPC				
Int. Cl. ⁵ : C08G 18/48, C08K 5/00, C08L 71/02, 75/08, 101/00, C09D 5/18, C09K 21/08, 21/12, D06M 13/156, 13/298 // (C08G 18/48, 101/00) (C08K 5/00, 5:13, 5:53, 5:5337)				
II. FIELDS SEARCHED				
Minimum Documentation Searched 7				
Classification System	Classification Symbols			
IPC	C08G 18/48, 101/00, C08K 5/00, 5:13, 5:53, 5:5337, C08L 71/02, 75/08, 101/00, C09D 5/18, C09K 21/08, 21/12, D06M 13/156, 13/198			
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched 8				
AU : IPC as above				
III. DOCUMENTS CONSIDERED TO BE RELEVANT 9				
Category*	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages 12	Relevant to Claim No 13		
X	EP.A, 83796 (BAYER AG et al) 20 July 1983 (20.07.83) See pages 1-8 and page 19 lines 10-14	(1,6-24)		
X	AU,A, 86710/75 (GENERAL ELECTRIC) 26 May 1977 (26.05.77) See entire document	(1,6-24)		
X	US,A, 3598733 (HINDERSTIN et al) 10 August 1971 (10.08.71) See entire document	(1,6-24)		
Y	US,A, 3715310 (BUTCHER) 6 February 1973 (06.02.73) See entire document	(1,4,6-24)		
Y	US,A, 4788238 (TODTEMANN et al) 29 November 1988 (29.11.88) See column 3 lines 30-67, claims 1-2	(1,4,6-24)		
(continued)				
<p>* Special categories of cited documents: 10</p> <table style="width: 100%;"> <tr> <td style="width: 50%;"> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </td> <td style="width: 50%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"Z" document member of the same patent family</p> </td> </tr> </table>			<p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"Z" document member of the same patent family</p>
<p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"Z" document member of the same patent family</p>			
IV. CERTIFICATION				
Date of the Actual Completion of the International Search 9 October 1990 (09.10.90)		Date of Mailing of this International Search Report 12 October 1990		
International Searching Authority Australian Patent Office		Signature of Authorized Officer  T. NIZNIK		

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

Y	GB,A, 2089350 (CIBA-GEIGY AG) 23 June 1982 (23.06.82) See entire document	(1,4,6-24)
Y	Patents Abstracts of Japan, C 78, page 758, JP,A, 53-27643 (ASAHI GLASS K.K.) 15 March 1978 (15.03.78) See entire abstract	(1,4,6-24)

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE 1

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claim numbers ..., because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claim numbers , because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claim numbers ..., because they are dependent claims and are not drafted in accordance with the second and third sentences of PCT Rule 6.4 (a):

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING 2

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.
2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

- ☐ The additional search fees were accompanied by applicant's protest.
☐ No protest accompanied the payment of additional search fees.

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON
INTERNATIONAL APPLICATION NO. PCT/AU 90/00275

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Members		
EP	83796	JP 58122957		
AU	86710/75	DE 2554324 JP 51082343	FR 2303049 JP 59098158	GB 1526068
US	4788238	DE 3444868 JP 61138657	EP 188683	ES 549148
GB	2089350	EP 54518	JP 57125258	

END OF ANNEX